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A Simple Route for Highly Luminescent Quaternary Cu-Zn-In-S Nanocrystal Emitters

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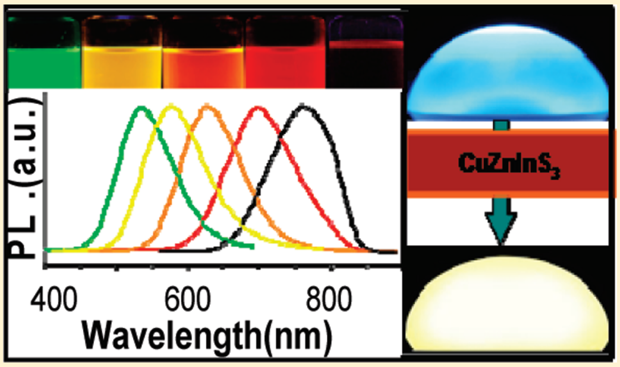
S *Supporting Information*

ABSTRACT: We reported a simple synthetic method for Cu−Zn−In−S nanocrystals (NCs) using commercially available, low toxic precursors. The various sizes and composition of Cu−Zn−In−S NCs were well controlled by simply changing reaction temperature and the ratio of the precursors, respectively. Accordingly, as produced these particles exhibited tunable photoluminescence (PL) spectra with emission color tuned from visible to the NIR region and had a relatively high QY of over 70% without coating any wide band gap shell materials. Further experimental results revealed that Cu−Zn−In−S NCs showed some advantages in contrast to typical plain II−VI and III−V semiconductor NCs. Preliminary tentative application on the preparation of QD-LEDs verified the feasibility in the lighting field.



KEYWORDS: nanocrystals, Cu-Zn-In-S, semiconductor, photoluminescence, LED

INTRODUCTION

Luminescent colloidal semiconductor nanocrystals (NCs) are of significant technology interests as they impact many applications including light emitting diodes (LEDs),[1−3] biomedical labeling,[4,5] lighting,[6−8] etc. Most of the existing examples of binary light emitting semiconductor NCs such as II−VI,[9,10] II−V,[11,12] and III−V[13−16] suffer from a number of disadvantages such as containing highly toxic elements, using extremely expensive and hazard raw materials, and needing surface modification to improve their emission efficiencies and stabilities. As a new kind of nanomaterial, I−III−VI semiconductor NCs such as $CuInS_2$ have been successfully prepared recently due to their avoidance of some of disadvantages as described above.[17−21] The progress on the synthesis of such NC emitters brought the quality of I−III−VI NCs, especially the optical properties (quantum yield of about 5%), to a level not comparable to that of CdSe NCs, although the emissive efficiency of NCs reported in the NIR region could be greatly improved by preparing their core/shell structures.[22,23] Therefore, such low reported quantum yield $CuInS_2$ NCs emitting in the visible region (500−650 nm) are not suitable for special applications such as display and lighting where fluorescence is very important. There is still a need to develop alternative novel NCs that are brightly and stablly fluorescing and soluble in most common solvents.

It has been proved that Cu-Zn-In-S semiconductor NCs have the tuned band gaps by changing not only the particle size but also the compositions of particles. The Bohr radius of bulk ZnS and $CuInS_2$ is 2.5 and 4.0 nm, respectively. This fact tells us that the size of Cu-Zn-In-S NCs below the Bohr exciton radius would show novel opto-electronic properties. So far, reports on colloidal Cu-Zn-In-S NCs have been rather limited, most likely owing to a lack of appropriate synthetic approaches. A pioneer work on the preparation of colloidal Cu-Zn-In-S NCs was reported by Lu's group where $CuZnInS_3$ NCs with different crystal structures (zinc blend and wurzite) were successfully prepared by thermolysis of the coprecursors $Zn(dedc)_2$, $In(dedc)_3$, and $Cu(dedc)_2$, and still, no photoluminescence (PL) has been investigated from these NCs.[24−26] Compared to the binary semiconductor NCs reported in the literature, the ability to control the size, size distribution, and optical properties of I-II-III-VI Cu-Zn-In-S NCs is still limited.

Here, we report the synthesis of colloidal Cu-Zn-In-S NCs with various sizes and stoichiometries by using commercial precursors (copper acetate, zinc acetate, indium acetate, and sulfur powder) (see Experimental Section). The synthetic scheme developed for Cu-Zn-In-S NCs was based on the reaction-controlled model in which the sizes of the NCs were dependent on the reaction temperatures. It was identified that reaction temperature higher than 140 °C was necessary to ensure the formation of homogeneous Cu-Zn-In-S nuclei and avoid producing phase impurities such as Cu_2S, In_2S_3, and/or ZnS (see Supporting Information, Figure S1−S3).

Figure 1 (A, B, and C) shows transmission electron microscope (TEM) images of the $CuZnInS_3$ NCs prepared under 180, 210, and 240 °C. The as-prepared NCs are nearly spherical in

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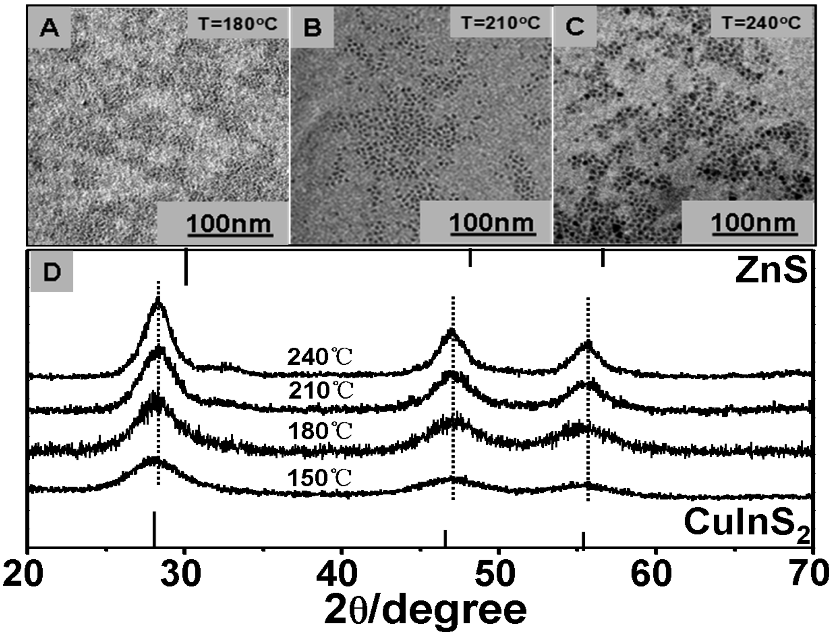
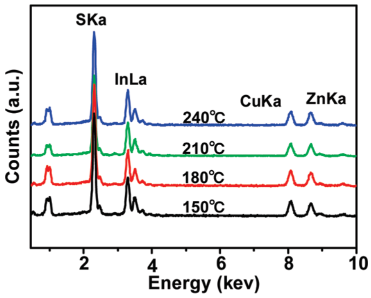


Figure 1. TEM images of $CuZnInS_3$ NCs prepared under different reaction temperatures, (A) 180 °C, (B) 210 °C, (C) 240 °C, and the corresponding X-ray diffraction patterns of NCs (D).



Element	AT%			
	150	180	210	240
S	50.8	50.8	50.4	50.0
In	17.0	16.2	16.8	17.0
Cu	16.1	16.7	16.2	16.5
Zn	16.1	16.4	16.6	16.5

Figure 2. EDS spectra (top) and the calculated atomic ratio (AT) (bottom) of the Cu-Zn-In-S NCs obtained under different reaction temperatures.

shape with narrow size distribution (∼10%) and reveal a high crystallinity with continuous lattice fringes throughout the whole particle by high resolution TEM measurements (see Figure S2, Supporting Information). Sizes of the NCs prepared under 180, 210, and 240 °C were about 3.0, 5.0, and 7.0 nm, respectively, showing an increase in size with the elevated reaction temperatures. All of the three samples presented the same diffraction peaks in X-ray powder diffraction (XRD) patterns (Figure 1D), indicating that all of the NCs possess the same crystal structure (zinc blend). The diffraction peaks are almost kept constant, which indicates that the NCs have the same composition. Energy dispersive X-ray spectroscopy (EDS) shown in Figure 2 was further employed to determine the elemental ratios of the NCs. It was identified that the chemical compositions of these NCs were almost ideal stoichiometries (Cu:Zn:In:S = 1:1:1:3), which was consistent with the ratios of the precursors used.

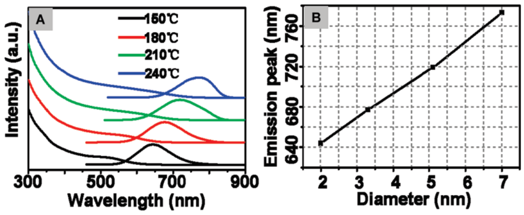


Figure 3. Absorption and emission spectra of as-prepared $CuZnInS_3$ NCs under different reaction temperatures (A). Relationship between the emission peak position and the size of $CuZnInS_3$ NCs (B).

Figure 3A shows absorption and emission spectra of the Cu-Zn-In-S NCs prepared under the different reaction temperatures. No well-defined exciton absorption peaks were observed for all the samples, although the particles had a good size distribution as shown in Figure 1A−C. It is documented that the broad absorption peaks observed in ternary and quaternary NCs should be attributed to their inhomogeneity of elemental distribution in one particle, which results in different crystal structures with various band gaps.[27] Experimental results indicated that absorbance of the Cu-Zn-In-S NCs were almost unchanged after the starting point-injection of the sulfur precursor solution. Detailed studies revealed that the absorption spectra of the NCs synthesized at the two different reaction temperatures shown in Figure 4 were almost constant from the starting point-injection of the sulfur precursor solution under the same conditions. Furthermore, the size of NCs was kept constant with increased reaction time. These experimental results showed that the composition of particles is completely the same during the reaction. Therefore, we conclude that homogeneous nuclei formed for all the elements. The absorption band edges of the resulting NCs shifted to longer wavelengths with increased reaction temperatures,

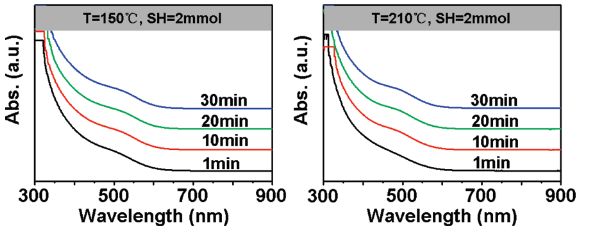


Figure 4. Evolution of UV−vis spectra of the NCs prepared at 150 °C (left) and 210 °C (right).

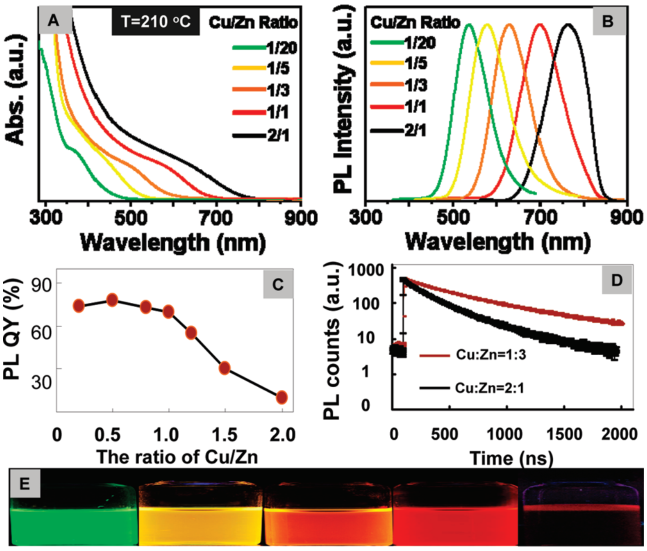


Figure 5. (A) Absorption and (B) emission spectra of the Cu-Zn-In-S NCs with different Cu/Zn ratios prepared under 210 °C. (C) PL QY of the plain NCs vs the ratio of Cu to Zn. (D) PL lifetime decays of two typical samples with Cu to Zn ratios of 1:3 and 2:1 under excitation wavelengths of 405 nm. (E) Digital pictures of the samples with different Cu/Zn ratios were taken under a 365 nm UV lamp (from left to right,1:20, 1:5, 1:3, 1:1, and 2:1).

meaning increased sizes of the NCs with elevated temperatures. From this point view, in this present synthetic approach, the sizes of the NCs were controlled by the reaction temperature[16] but not the reactivity of the precursors.[28] Interestingly, the Cu-Zn-In-S NCs exhibited strong band edge luminescence which could be tuned by changing the particle sizes. Figure 3B gives a variation of emission peak positions of the NCs with their sizes. The emission of the NCs was tunable in the region from 620 to 750 nm by increasing the size of the NCs from 2.0 to 7.0 nm.

Figure 5A shows the absorption spectra of NCs prepared by changing molar ratios of the precursors while keeping the other reaction conditions unchanged. The absorption band edges of the resulting NCs shifted gradually from UV−vis to NIR with increasing the ratio of Cu/Zn from 1:20 to 2:1. TEM observation indicated that all of the samples had a similar particle size, which excluded the size effect on the shift of the band edges. Crystal structures of the NCs were determined by the XRD patterns shown in Figure 6 where all NCs showed a similar zinc blend structure, and their diffraction peaks systematically shifted toward higher angles with decreasing the Cu/Zn ratio from 2:1 to 1:20. The continuous peak-shift of the NCs reveals that no phase separation and separated nucleation happened in the current synthetic approach, suggesting the formation of Cu-Zn-In-S NCs.[29,30] Quantitative elemental analyses of the NCs by EDX further revealed that the compositions of the NCs were well consistent with the molar ratios of the precursors used (Figure S5 and Table S1, see Supporting Information). Thus, the shift of the absorption band edges should be attributed to variation in composition of the NCs. Accordingly, PL emissions of the NCs were successfully tuned in the range from UV−vis to NIR by only changing the Cu:Zn ratios from 1:20 to 2:1 (Figure 5B). Figure 5C gives the PL QY of the plain NCs with different Cu:Zn ratios. The plain NCs presented an almost constant high QY of 70% when the ratios of Cu:Zn were in the range from 1:20 to 1:1, and then decreased gradually when the ratios were higher than 1:1. PL dynamics of two typical samples with Cu:Zn ratios of 1:3 and 2:1 were investigated to understand the mechanism underlying the decreased QY with increased Cu:Zn ratios. For the sample with Cu:Zn raio of 2:1, its PL decay curve can be fitted by a multi-exponential, resulting from imperfect crystal structures in the NCs induced by Cu interstitials produced under anion deficient conditions.[18] On the contrary, the sample with a Cu:Zn ratio of 1:3 almost showed a single exponential PL decay, suggesting extensive elimination of the internal defects and thus a suppressed nonradiative recombination process.[23] As a result, the plain NCs presented an emission efficiency as high as 70%, which was comparable to those of core/shell NCs based on CdSe.[31]

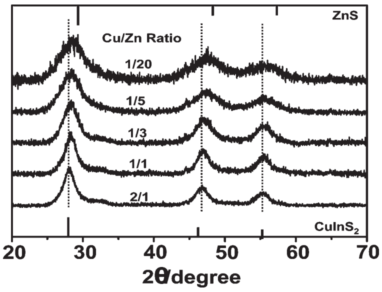


Figure 6. XRD patterns of the Cu-Zn-In-S NCs with different compositions. The reaction temperature was set at 210 °C.

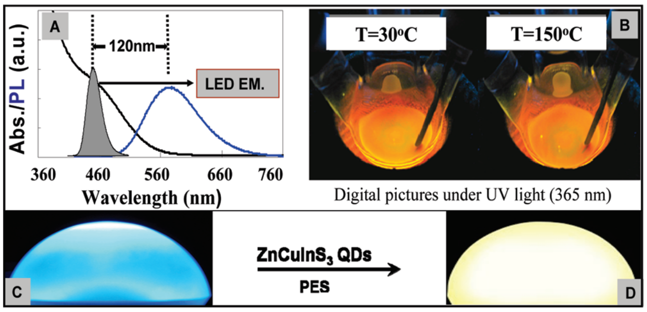


Figure 7. Absorption (dark line) and emission (blue) spectra of a typical Cu-Zn-In-S sample and LED emission at ∼460 nm (A). Digital pictures of Cu-Zn-In-S NCs heated to the different temperatures under UV light (365 nm) (B). Digital pictures of LEDs before (C) and after (D) being coated by the Cu-Zn-In-S NCs.

The as-prepared Cu-Zn-In-S NCs were substantially stable in two months when being stored under ambient conditions (Figure S6, see Supporting Information). In addition, the NCs showed unique advantages such as large Stoke's shift (∼120 nm)

(Figure 7A) and good thermal stability (Figure 7B), where the Cu-Zn-In-S NCs did not show any significant change in emission intensity upon heating to 150 °C by visual observation. The outstanding thermal stability of the NCs further implies that these multinary particles are more suitable for some special technical applications than are the corresponding q-dots such as CdSe or InP where they show strong self-absorbance and poor thermal stability, for which high temperature is inevitable, such as solid-state lighting, lasers and LEDs. To assess the suitability of the NCs as optically active centers, a simple lighting device was fabricated by using the commercial blue−white LEDs coated by Cu-Zn-In-S NC film (see Supporting Information, Figure S7). The NCs with a Cu:Zn ratio of 1:5 with the emission wavelength at 580 nm were employed since their absorption shoulder (∼460 nm) matched the emission of the commercial blue−white LEDs (Figure 7A). Figure 7C and D shows the digital pictures of the LED before and after being coated with typical Cu-Zn-In-S NCs. The color of the LEDs was transformed from cool blue light into warm yellow light as the LED's emission passed through the NC film.

In summary, we developed a simple synthetic method for Cu-Zn-In-S NCs containing commercially available, low toxic precursors. The new synthetic approach indicated that the size and composition of Cu-Zn-In-S particles could be well controlled by simply changing reaction temperature and the ratio of the precursors, respectively. As a result, the NCs produced exhibited not only broad PL spectra with emission color tuned from visible to NIR region by changing the sizes or/and composition but also high QY of over 70% without coating the wide band gap shell materials. Further experimental studies revealed that these Cu-Zn-In-S NCs showed some advantages in contrast to other semiconductor NCs such as long PL lifetime, large Stoke's shifts, and excellent chemical and thermal stability. Preliminary tentative applications of these Cu-Zn-In-S NCs showed the feasibility in lighting by preparation of QD-LEDs, which will further promote the applied progress of NCs in some fields such as display and solid-state lighting.

EXPERIMENTAL SECTION

Materials and Methods. *Materials.* Technical grade (90%) octadecene (ODE), indium acetate (In(Ac)3, 99.99%), copper (II/I) acetate (99.99%), oleic acid (90%), and zinc acetate (99.99%) were purchased from Alfa. Oleylamine (97%), dodecylthiol (99.9%), and sulfur powder (S, 9.999%) were purchased from Aldrich.

Methods. In a typical synthesis of $CuZnInS_3$ NCs, zinc acetate (0.0176 g, 0.1 mmol), indium acetate (0.0292 g, 0.1 mmol), 1-dodecanethiol (DDT, 2 mmol), oleic acid (0.6 mmol), and copper(I) acetate (0.0190 g, 1 mmol) were mixed with ODE (4 mL) in a three-necked flask. The reaction mixture was degassed under vacuum for 1 min and purged with argon. The flask was heated to 210 °C until a clear solution was formed, and then sulfur solution (0.3 mmol) dissolved in 0.5 mL oleylamine was quickly injected into the reaction solution. After being kept at definite temperatures (150, 180, 210, or 240 °C) for 10 min, the solution was heated at 230 °C for another 5 min and then cooled to room temperature. For purification, 10 mL of hexane was added, and byproducts were removed by successive methanol extraction until the methanol phase was clear. For syntheses of the Cu-Zn-In-S NCs with various compositions, only the ratio of precursors used was different while keeping the other reaction conditions unchanged.

Characterizations. TEM observations were taken on a JEOL 100CX transmission electron microscope with an acceleration voltage of 100 kV. Carbon coated copper grids were dipped in the hexane solutions to deposit the NCs onto the films. X-ray powder diffraction (XRD) patterns were obtained by using a Philips PW1830 X-ray diffractometer. Elemental compositions of NCs were determined by energy-dispersive spectroscopy. UV−visible spectra were recorded on an HP8453 UV−visible spectrophotometer. PL spectra and PL dynamics were taken on an FS900 steady-state fluorescence spectrometer and a Spex Fluorolog 112 spectro-fluorometer, respectively. PL quantum yields (QYs) of the samples were determined using organic dyes (R640, emission at 570 nm, QY = 100%) or standard CdSe quantum dots (emission at 575 nm, QY = 70%, emission at 615 nm, QY = 80%) as standards.

ASSOCIATED CONTENT

Supporting Information. Supporting results mentioned in the text (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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